

DEFOLIANTS

For several reasons, only a small number of compounds are registered as defoliants. First, only a few crops require defoliation. Second, the materials must act rapidly to bring about abscission within a minimum time after application. Third, the compounds must break down rapidly, leaving no undesirable residue in the target portion of the crop. Defoliants are not for lawn and garden use.

Inorganic Salts

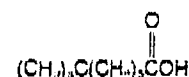
The inorganic salts are the oldest defoliants. Sodium chlorate (NaClO_3), magnesium chlorate ($\text{Mg}(\text{ClO}_3)_2 \cdot 6\text{H}_2\text{O}$), disodium octaborate tetrahydrate ($\text{Na}_2\text{B}_8\text{O}_{14} \cdot 4\text{H}_2\text{O}$), and the other sodium polyborates are good examples of these old standbys, which are still used, primarily on cotton. These are contact materials that, by virtue of their high acidity, bring about rapid destruction of the delicate protoplasmic structures, resulting in the formation of the petiole abscission layer. The exact nature and sequence of the chemical reactions are unknown. The chlorates cause chlorosis of leaves and a starch depletion in stems and roots when applied in less than lethal doses.

Aliphatic Acids

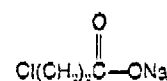
As indicated in Chapter 11, an aliphatic acid is a carbon-chain acid. Their sodium salts are also included in this group. Neodecanoic acid is a readily degradable compound of moderate effectiveness for use on most crops requiring defoliation.

Prep® is the sodium salt of an aliphatic acid, is used as a defoliant for cotton and potatoes, and is rapidly absorbed but not translocated.

NEODECANOIC ACID



Prep®



sodium *cis*-3-chloroacrylate

Paraquat

Paraquat—also mentioned in Chapter 11 in the bipyridylium class—damages plant tissue very rapidly. Its swift action results from the breakdown of plant cells responsible for photosynthesis, giving the leaves a waterlogged appearance within a few hours of treatment. Paraquat results in the formation of OH^\cdot radicals or hydrogen peroxide (H_2O_2) as the primary toxicant(s). Because most leaves drop off, paraquat is considered a defoliant.

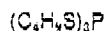
PARAQUAT



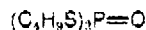
1,1'-dimethyl-4,4'-bipyridylium ion
(dichloride)

Organophosphates

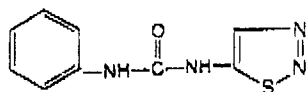
Merphos and DEF® are two organophosphate defoliants that have proved extremely useful in cotton production. Neither of these compounds is hormone acting. Rather, they induce abscission by injur-

MERPHOS (Felex[®])

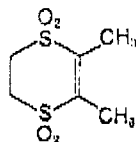
S,S,S-tributyl phosphorotriothioate

DEF[®]

S,S,S-tributyl phosphorotriphosphate

THIDIAZURON (Dropp[®])

N-phenyl-N'-1,2,3-thiadiazol-5-ylurea

Harvade[®]

2,3-dihydro-5,6-dimethyl-1,4-dithiin 1,1,4,4-tetraoxide

ARSENIC ACID

ing the leaf, causing changes in the levels of naturally occurring plant hormones that induce the early formation of the leaf abscission layer. Defoliation follows treatment by 4 to 7 days.

Miscellaneous Defoliants

Two very new defoliants, thidiazuron and Harvade[®] are still in the testing and registration stages at this writing. Thidiazuron is a defoliant for cotton that stimulates the formation of the abscission layer, causing shedding of the leaves, and also inhibits regrowth of leaves on treated cotton plants. Harvade[®] is an effective cotton defoliant even at temperatures of 21°C and below. It also defoliates nursery stock, grapes, and natural rubber. With rice and sunflower it has been shown to enhance maturation and subsequently reduce seed moisture content.

DESICCANTS**The Inorganics**

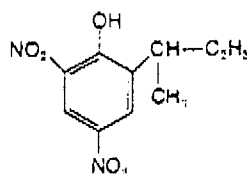
The number of desiccants available is much larger than the number of defoliants. Ammonia and ammonium nitrate are both used as desiccants for cotton; they also ultimately add nutrients to the soil after the crop residue is returned to the soil. Petroleum solvents are applied to alfalfa and clover seed crops as well as to potatoes to enhance leaf drying and harvest.

Two of the inorganic salts mentioned in earlier chapters are used as desiccants for cotton: sodium borate(s) and sodium chlorate.

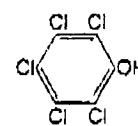
Arsenic acid is probably the oldest of the cotton desiccants, and it is still used in quantity. The material penetrates the leaf cuticle and the rapid contact injury precludes any extensive translocation. Arsenic acid uncouples oxidative phosphorylation and forms complexes with —SH-containing enzymes.

Phenol Derivatives

Dinoseb and pentachlorophenol, both phenol derivative herbicides of universal effectiveness, are used as desiccants for cotton. Pentachlorophenol has additional uses on seed crops of alfalfa, clovers, lespedeza, and vetch.

DINOSEB

2-sec-butyl-4,6-dinitrophenol

PCP

pentachlorophenol

Common name, trade name, and basic manufacturer(s)	Chemical name	General use pattern	Oral LD ₅₀ (rats)	Dermal LD ₅₀ (rabbits)
cycloate, Ro-Neet [®] (Stauffer)	S-ethyl N-ethylthiocyclohexanecarbamate	Preplant herbicide for grass, broad-leaf weeds in sugar beets, table beets, spinach.	3160	>4640
2,4-D, several (several)	(2,4-dichlorophenoxy)acetic acid	Selective broad-leaf weed control in monocots (small grains, corn, sorghum, sugarcane), noncrop areas.	375	—
Dacthal [®] (see DCPA)				
dalapon, Dowpon [®] (Dow; Diamond Shamrock)	2,2-dichloropropionic acid (sodium salt)	Systemic herbicide for various grasses and rushes in crop, noncrop areas.	6500	10,000
dazomet, Mylone [®] (Hopkins; Stauffer)	tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione	Preplanting seedbed treatment for tobacco, turf, ornamentals; antimicrobial in glues for paper products; nematocide, silicide.	500	—
2,4-DB, several (several)	4-(2,4-dichlorophenoxy)butyric acid	Selective control of certain broad-leaf weeds in alfalfa, clover, soybeans, peanuts.	500	>10,000
DCPA, Dacthal [®] (Diamond Shamrock)	dimethyl tetrachloroterephthalate	Preemergence herbicide for grass, broad-leaf weeds in soybeans, cotton, seeded vegetables.	>3000	>10,000
DEF [®] (Mobay)	S,S,S-tributylphosphorotrithioate	Defoliant for cotton.	200	>1000
desmidipham, Betanex [®] (NOR-AM)	ethyl m-hydroxycarbanilate carbanilate (ester)	Broad-leaf weed control in sugar beets.	>9600	>2000
Destun [®] (see perfluidone)				
Devine [®] (see Phythophora palmivora)				
Devrinol [®] (see napropamide)				
diallate, Avadex [®] (Monsanto)	5-(2,3-dichloroallyl)diisopropylthiocarbamate	Soil-incorporated preemergence control of wild oats in several crops.	395	2000
dicamba, Banvel [®] , Banex [®] , Bush Buster [®] (Velsicol)	3,6-dichloro-o-anisic acid	Controls annual, perennial weeds in corn, sorghum, small grains; pasture, rangeland, noncropland.	1040	>2000
dichlobenil, Casoron [®] (Thompson-Hayward)	2,6-dichlorobenzonitrile	Selective weed control in ornamentals, orchards, vineyards; total weed control for industrial sites.	3160	1350
dichlorprop, several (several)	2-(2,4-dichlorophenoxy)propionic acid	Systemic brush control on rights-of-way, rangeland; broad-leaf weeds in cereals.	400	1400
diclofop methyl, Hoelon [®] (American Hoechst)	methyl 2-[4-(2',4'-dichlorophenoxy)-phenoxy] propanoate	For annual weed grasses (wild oats) in wheat, barley, soybeans.	679	>2000
diethylat ethyl, Antor [®] (BFC Chemicals)	N-chloroacetyl-N (2,6-diethylphenyl)glycine ethyl ester	Preplant preemergence for control of annual grass, broad-leaf weeds in sugar beets, soybeans.	2300	4000
difenzoquat, Avenger [®] (American Cyanamid)	1,2-dimethyl-3,5-diphenyl-1H-pyrazolium methyl sulfate	Postemergence for controlling wild oats in wheat, barley.	270	3540
Dinitro [®] (see dinoseb)				
dinoseb, DNBP, Dinitro [®] (several)	2-sec-butyl-4,6-dinitrophenol	General contact herbicide, desiccant.	40	75

The most valuable, and produced in the greatest quantity, were chlordane and dieldrin. Structures of the common cyclodienes are presented to illustrate their similarity and complexity.

The nomenclature and chemistry of the cyclodienes are rather complicated. The cyclodienes have three-dimensional structures and thus possess stereoisomers; that is, forms that have the same kinds and numbers of atoms, but their atoms differ in their spatial location and structure. For instance, endrin is a stereoisomer of dieldrin.

The cyclodienes have about equal toxicity or toxic effects on insects, mammals, and birds. They are, however, much more toxic to fish, perhaps because when the compound is introduced into water the fish continually respire and ingest any toxic compound contained in their aquatic environment.

The modes of action of the cyclodienes are not clearly understood. It is known that they are neurotoxicants that have effects similar to those of DDT and HCH. They appear to affect all animals in generally the same way, first with nervous activity followed by tremors, convulsions, and prostration. The cyclodienes undoubtedly disturb the delicate balance of sodium and potassium within the neuron but in a way differing from that of DDT and HCH.

Polychloroterpene Insecticides

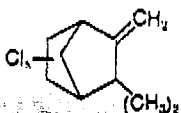
There are only two polychloroterpene materials, toxaphene, discovered in 1947, and strobane, introduced in 1951. Neither have ever been considered urban insecticides. Toxaphene is manufactured by the chlorination of camphene, a pine tree derivative.

Toxaphene had by far the greatest use of any single insecticide in agriculture. It was used on cotton, first in combination with DDT, for alone it has a low order of toxicity to insects. In 1965, after several cotton insects became resistant to DDT, toxaphene was formulated in combination with methyl parathion, an organophosphate insecticide discussed later in this chapter. As late as 1976 some 11.8 million kg of toxaphene was used on cotton, or 41 percent of all insecticides used on cotton that year.

Toxaphene is an amazing mixture of more than 177 polychlorinated derivatives, which are 10-carbon compounds including Cl_6 , Cl_7 , Cl_8 , Cl_9 , and Cl_{10} constituents. Most are probably isomeric Cl_7 -, Cl_8 -, and Cl_9 -bornanes. No single component makes up more than a small percentage of the technical mixture. The toxaphene components of greater concern are those most toxic to mammals and fish. One of these is toxicant A, shown in its three-dimensional form (Saleh and Casida, 1978). Toxicant A makes up only 3 percent of technical toxaphene, but it is 18 times more toxic to mice, 6 times more toxic to houseflies, and 36 times more toxic to goldfish than technical toxaphene.

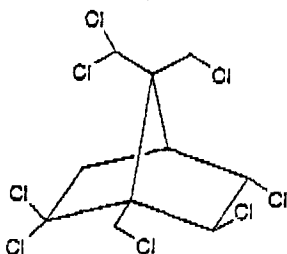
These materials are persistent in the soil, though not as persistent as the cyclodienes, and disappear in three to four weeks from the surfaces of most plant tissues. This disappearance is attributed more to volatility than to actual metabolism or photolysis (disintegration from the effects of ultraviolet light in sunlight). They are fairly easily metabolized by mammals and birds, and are not stored in body fat to

TOXAPHENE



chlorinated camphene containing 67 to 69 percent chlorine

TOXAPHENE TOXICANT A



2,2,5-endo,6-exo,8,9,9,10-octachlorobornane
 $\text{C}_{10}\text{H}_6\text{Cl}_8$

CHLORINATED INSECTICIDES

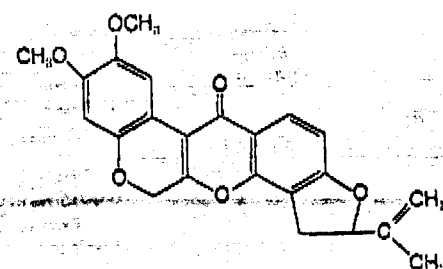
Many of the organochlorine insecticides were, early in their use history, found to be extremely toxic to fish and were in a few cases used as piscicides. Among these were toxaphene, beginning in 1948, endrin in 1952, and endosulfan (Thiodan®) in 1960. Their use was usually catastrophic, since they are toxic to all forms of wildlife and very persistent. Consequently, none of the three were ever registered for use. (Endrin gained a bad reputation in the Mississippi River fish kills of the mid 1960s, as did endosulfan in the accidental fish kill in the Rhine River in 1969.) Needless to say, none of the organochlorine insecticides should be used as piscicides.

ROTENONE

Rotenone is the most useful piscicide available for reclaiming lakes for game fishing. It eliminates all fish, closing the lake to reintroduction of rough species. After treatment, the lake can be restocked with the desired species. Rotenone is a selective piscicide, in that it kills all fish at dosages that are relatively nontoxic to fish food organisms. It also breaks down quickly, leaving no residues harmful to fish used for restocking. The recommended rate is 0.5 ppm or 5.1 kg per hectare-meter of water (1.36 pounds per acre-foot).

Rotenone is a strong inhibitor of the respiratory chain in fish, and the site of action is located in the flavoprotein region of this chain. The specialized structure of the gills favors passage of rotenone into the blood, which is then transported to vital organs for respiration inhibition.

ROTENONE



ANTIMYCIN®

Antimycin® is actually an antibiotic, produced by the fungus *Streptomyces*, whose fish poison characteristics were discovered in 1963. In the dosages used, it is specific for fish, leaving unharmed other aquatic life, waterfowl, and mammals. It is lethal in small concentrations to all stages of fish, egg through adult. It passes into the blood through the gills and irreversibly blocks cellular respiration at the cytochromes, thus inhibiting oxidative phosphorylation. Because it is not repellent to fish, it is the first piscicide to be successfully used as spot treatments in lakes. It degrades rapidly in water, usually within a few days, and even faster if the pH of the water is high. Antimycin®, also sold under the name of Fintrol®, is formulated as a 1 and 5 percent wettable powder and as a 10 percent solution, and must be used under technical supervision of state and federal fish and game agencies.